

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11) EP 0 801 027 A1

(12)

EUROPEAN PATENT APPLICATION

published in accordance with Art. 158(3) EPC

(43) Date of publication:

15.10.1997 Bulletin 1997/42

(51) Int. Cl.⁶: C01B 39/36, C01B 39/04,
B01J 29/04

(21) Application number: 95941571.2

(86) International application number:
PCT/CN95/00099

(22) Date of filing: 25.12.1995

(87) International publication number:
WO 96/20891 (11.07.1996 Gazette 1996/31)

(84) Designated Contracting States:
FR GB

(30) Priority: 30.12.1994 CN 94113403

(71) Applicants:

- CHINA PETRO-CHEMICAL CORPORATION
Beijing 100029 (CN)
- DALIAN INSTITUTE OF CHEMICAL PHYSICS,
CHINESE ACADEMY OF SCIENCES
Dalian City, Liaoning Province 116023 (CN)
- Fushun Petro-chemical Company, Sinopec
Xinfu District, Fushun,
Liaoning Province 113004 (CN)

(72) Inventors:

- WANG, Qingxia
Liaoning Province 116023 (CN)

- ZHANG, Shurong
Liaoning Province 113004 (CN)
- CAI, Guangyu
Liaoning Province 116023 (CN)
- LI, Feng
Liaoning Province 113004 (CN)
- XU, Longya
Liaoning Province 116023 (CN)
- HUANG, Zuxian
Liaoning Province 113004 (CN)
- LI, Yuying
Liaoning Province 113004 (CN)

(74) Representative: Brown, John David
FORRESTER & BOEHMERT
Franz-Joseph-Strasse 38
80801 München (DE)

(54) RARE EARTH-ZSM-5/ZSM-11 COCRYSTALLINE ZEOLITE

(57) A rare earth-containing zeolite with a cocrystal-
line structure of ZSM-5 and ZSM-11, wherein the weight
ratio of the moiety having the crystalline structure of
ZSM-5 to the moiety having the crystalline structure of
ZSM-11 is 0.1 to 10, which has, in the sodium form, the
X-ray diffraction pattern set forth in Table 1, and in its
originally synthesized anhydrous state, a chemical for-
mula in terms of mole ratios of oxides as follows: $0.1-1.0$
 $\text{Na}_2\text{O} \cdot 0.01-1.0 \text{ RE}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3 \cdot 20-300 \text{ SiO}_2$. Said
zeolite has good acid hydrothermal stability and resist-
ance against impurity contamination, and is useful as
catalyst in various hydrocarbon conversions.

EP 0 801 027 A1

Description**Field of the Invention**

5 The present invention relates to a crystalline aluminosilicate zeolite, the preparation process and the use thereof. More specifically, the present invention relates to a rare earth-containing aluminosilicate zeolite with a cocrystalline structure of ZSM-5 and ZSM-11, a process for preparing the same, and the use of said zeolite in the catalytic conversion of hydrocarbons.

Background of the Invention

Zeolite ZSM-5 is a kind of high silicon zeolite with Pentasil structure developed by Mobil Oil Corporation (USP 3,702,886) and is widely used as catalytic material in isomerization, disproportionation, catalytic cracking and catalytic dewaxing due to its unique pore structure. USP 4,107,224 discloses a process for preparing ethylbenzene by the alkylation of benzene with ethylene utilizing zeolite ZSM-5 catalyst, wherein the raw material ethylene needs to be diluted with inert hydrocarbons. For the sake of industrial application, diluted ethylene is obtained from the tail gases of some devices in an oil refinery, such as dry gas of catalytic cracking, coke oven gas and the like. However, when such tail gases are used as sources of diluted ethylene, they require to be pretreated to remove the impurities therein such as hydrogen sulfide, water, carbon dioxide and the like until the contents of them are below 10 ppm.

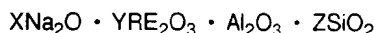
20 Zeolite having a structure intermediate that of ZSM-5 and ZSM-11 (hereafter referred to as a ZSM-5/ZSM-11 intermediate), another zeolite product developed by Mobil Oil Corporation (USP 4,229,424), is prepared by using quaternary ammonium salt as template. The ZSM-5/ZSM-11 intermediate has a characteristic X-ray diffraction pattern and such structures intermediate that of ZSM-5 (designated as I) and ZSM-11 (designated as S) as SISI, SSII, IISIIISI, SSSISI, IISISI, etc., and it has, in anhydrous state, a chemical formula in terms of mole ratios of oxides as follows: $0.9 \pm 0.3 M_{2/n}O : Al_2O_3 : ZSiO_2$, wherein M is a cation, preferably hydrogen or a hydrogen precursor, e.g., ammonium cation; n is the valence of the cation; and Z is at least 5 and may be up to 5000. It is taught in the patent that the cations in the zeolites can be replaced, at least in part, by ion exchange with other cations in accordance with techniques well-known in the art. USP 4,289,607 further discloses the use of said zeolite in catalytic reactions, such as the conversion of methanol to gasoline, oligomerization of olefins, alkylation of aromatics, isomerization of xylene, catalytic cracking of hydrocarbons and the like.

30 In general, incorporation of rare earth elements into zeolites will increase the activity and stability of the zeolites. For example, REY zeolites obtained by ion-exchange treatment of NaY zeolites with RE^{3+} cation have higher cracking activity and hydrothermal stability than those of NaY zeolites (USP 3,402,996). However, with respect to such high silicon zeolites as ZSM-5, ZSM-11 and ZSM-5/ZSM-11, due to their high silica to alumina ratio and therefore less electric charge centers and high hydrophobicity as well as smaller pore openings in the channel of zeolite, it is very difficult to incorporate such trivalent cations of large ionic radius as rare earth cations into the channel of those zeolites in aqueous medium by conventional ion-exchange techniques, thus RE^{3+} is less likely to coordinate with the electronegative centers of aluminium on the low density skeleton (P. Cho and F. G. Dwyer, ACS Symp. Ser., 218, 59-78, 1983). GB2,003,358A discloses the preparation of zeolite ZSM-5 containing metal, including trivalent metal, by adding salts of mineral acids including salts of trivalent metals to the raw materials of zeolite synthesis. And CN 89108836.9, CN 90104732.5 and USP 5,232,675 discloses the synthesis of high silicon ZSM-5 zeolites containing rare earth elements by employing rare earth-containing faujasite as crystal seed. So far, these have been the reports known to incorporate rare earth into ZSM-5 zeolite by synthesis instead of conventional ion-exchange techniques. But it has never been reported how a rare earth-containing zeolite with a cocrystalline structure of ZSM-5 and ZSM-11 can be directly synthesized.

45 An object of the invention is to provide a directly synthesized rare earth-containing zeolite with a cocrystalline structure of ZSM-5 and ZSM-11. Another object of the invention is to provide a process for preparing the zeolite. A further object of the invention is to provide uses of the zeolite in catalytic conversions.

Summary of the Invention

50 The zeolite provided by the invention is the one containing rare earth and having a cocrystalline structure of ZSM-5 and ZSM-11, wherein the weight ratio of the moiety having the crystalline structure of ZSM-5 to the moiety having the crystalline structure of ZSM-11 is 0.1-10, which has, in the sodium form, the X-ray diffraction pattern set forth in Table 1, and, in its originally synthesized anhydrous state, a chemical formula in terms of mole ratios of oxides as follows:



wherein $X=0.1-1.0$,

Y=0.01-1.0, and
Z=20-300.

The zeolite of the present invention is prepared in the presence of water glass, an aluminium source, a mineral acid and a salt of rare earth element by using C₂-C₈ diamine as template. The zeolite is useful as catalyst in alkylation of aromatics, aromatization of alkanes, conversion of methanol to light olefins and the like.

Detailed Description of the Invention

The zeolite of the invention contains a single rare earth element or a mixture thereof, and has a cocrystalline structure of ZSM-5 and ZSM-11, wherein the weight ratio of the moiety having the crystalline structure of ZSM-5 to the moiety having the crystalline structure of ZSM-11 is 0.1-10, whose chemical formula in its originally synthesized anhydrous state in terms of mole ratios of oxides is as follows:



wherein X=0.1-1.0,
Y=0.01-1.0, and
Z=20-300.

Like all of the other zeolites, the zeolite of the invention can have its sodium cations replaced by other cations by conventional ion-exchange techniques, that is, the as-synthesized Na-zeolite can be converted to other forms such as ammonium or hydrogen, zinc, gallium, magnesium form and the like by ion exchange techniques.

The zeolite of the invention has, in its sodium form, the X-ray diffraction pattern set forth in Table 1. The X-ray diffraction analysis was carried out in accordance with standard measuring technique by using radiation of K- α doublet of copper, wave filtration of nickel and a scintillation counter. The interplanar spacing (d) in the Table corresponding to each diffraction line was calculated according to Bragg Equation from the position of each diffraction peak (2 θ , wherein θ represents the Bragg angle) recorded on the chart. In the Table, the relative intensity, 100I/I₀, is the ratio of each diffraction peak height (i.e., diffraction intensity) I to the highest diffraction peak height (i.e., the strongest diffraction intensity) I₀ multiplied by 100, wherein VS (very strong) represents a relative intensity value of 100-60, S (strong) represents 60-40, M (medium) represents 40-20, and W(weak) represents less than 20.

Table 1

d (Å)	100I / I ₀
11.2±0.2	M
10.1±0.2	M
6.05±0.14	W
4.40±0.08	W
3.86±0.07	VS
3.72±0.07	S
3.65±0.07	W - M
2.01±0.02	W

Table 2 shows the X-ray diffraction pattern of the zeolite provided by the present invention together with that of the ZSM-5/ZSM-11 intermediate crystalline zeolite which has been granted the patent. It can be seen from Table 2 that there are some differences between the positions but significant differences between the relative intensities of the two groups of diffraction lines.

Table 2

d (Å)	ZSM5 / ZSM11 (USP4, 229, 424) 100I / I ₀	Zeolite of the Invention 100I / I ₀
11.2±0.2	VS	M
10.1±0.2	VS	M
6.73±0.14	W	—
6.05±0.14	—	W
4.63±0.08	W	—
4.40±0.08	—	W
3.86±0.07	S	VS
3.72±0.07	M - S	S
3.65±0.07	—	W - M
2.01±0.02	W	W

The zeolite of the invention has a surface area of 300 to 400 m²/g determined by BET low temperature nitrogen adsorption method. The adsorption capacities of the zeolite towards n-hexane and cyclohexane at 25 °C and a partial pressure of adsorbates of 20 mmHg are 9 to 11 % and 3 to 5% by weight, respectively, and the adsorption capacity of the zeolite towards water at 25 °C and a partial pressure of adsorbate of 12 mmHg is 4 to 8% by weight.

The zeolite of the invention is prepared in the presence of water glass, an aluminium source, a mineral acid and a salt of rare earth element by using C₂-C₈ diamine as template. More specifically, a zeolite product is obtained by mixing a homogeneous mixture I composed of water glass, a C₂-C₈ diamine and water with a homogeneous mixture II composed of an aluminium source, a mineral acid, a salt of rare earth element and water under vigorous stirring to form a gel, then crystallizing the gel under stirring at a temperature of 100 to 200 °C for 0.5 to 4 days, followed by rapidly cooling to room temperature and washing with deionized water until a pH of 8 to 9, and finally drying.

In the preparation process of the invention, said diamine is selected from any one or a mixture of two of C₂-C₈ primary diamines. Said aluminium source is selected from an aluminium salt of a mineral acid comprising aluminium chloride, aluminium bromide, aluminium nitrate, aluminium sulfate and aluminium phosphate. Said mineral acid is selected from a group comprising sulfuric acid, hydrochloric acid, nitric acid and phosphoric acid, preferably sulfuric acid. Said salt of rare earth element is preferably selected from a chloride, nitrate and sulfate salt of a single rare earth element or a mixture thereof.

In the process, the mole ratio of the above raw materials are as follows: Na₂O/Al₂O₃: 7-12; RE₂O₃/ Al₂O₃: 0.01-1.0; SiO₂/ Al₂O₃:30-600; H₂O / SiO₂: 20-100; amine / SiO₂: 0.1-0.5.

In the process of the invention, addition of a lower molecular weight diamine or a mixture thereof as template contributes to the increase of the ZSM-5 content in the cocrystalline zeolite. Furthermore, the ratio of ZSM-5 to ZSM-11 of the cocrystalline zeolite may be adjusted by changing crystallization temperature and controlling crystallization time.

The zeolite provided by the invention has good hydrothermal stability and resistance against contamination by impurities such as hydrogen sulfide, water, carbon monoxide and carbon dioxide. The zeolite of the invention can be further modified like other zeolites by conventional ion-exchange techniques to be provided with various catalytic properties and the modified zeolite, with the aid of suitable matrix, can be made into catalysts required by various processes. For example, the zeolite can be converted to hydrogen form by ion-exchanging with ammonium cations and heating, and used as catalyst for the alkylation of aromatics; and the zeolite can be converted to zinc or gallium form by ion exchanging with zinc or gallium cations and used as catalyst for the aromatization of alkanes; the zeolite can also be converted to magnesium form by ion exchanging with magnesium cations and used as catalyst for the conversion of methanol to light olefins. The zeolite can also be converted to other forms and used in other reactions such as hydrocarbon conversions, e.g. isomerization, cracking, disproportionation and the like.

Examples

The following examples will further illustrate the invention but they are not intended to limit the scope of the invention.

In the examples, the unit cell parameters and the weight ratio of the moiety having the crystalline structure of ZSM-

5 to the moiety having the crystalline structure of ZSM-11 of the zeolite products were determined by X-ray diffraction method. The contents of sodium and rare earth and the silica to alumina ratio were determined by atomic absorption spectrometry. The adsorption capacities towards n-hexane and cyclohexane were determined at 25 °C and a partial pressure of adsorbate of 20 mmHg. The adsorption capacity towards water was determined at 25 °C and a partial pressure of adsorbate of 12 mmHg.

Example 1

Preparation of the La - ZSM-5/ZSM-11 cocrystalline zeolite of the invention by using hexamethylene diamine as template

3000 ml water glass (containing 180g/l of SiO_2 ; 60g/l of Na_2O), 1900 ml of deionized water and 250g of 98% hexamethylene diamine were mixed homogeneously to give operating solution I.

51g of 97% $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, 400 ml of 4M H_2SO_4 , 35g of 99% $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$ and 2100 ml of deionized water were mixed homogeneously to give operating solution II.

The above two operating solutions were mixed under vigorous stirring to form a gel. The stirring was continued for another 30 minutes, then the rotation rate was lowered to about 100 rpm. Crystallization was carried out at 175 °C under stirring for 72 hours.

The material from crystallization was rapidly cooled to room temperature. The resulting crystal was washed with deionized water until the pH was washed to be 8 to 9, filtered, and dried at 110 ± 10 °C for 10 hours to give the La - ZSM-5/ZSM-11 cocrystalline zeolite.

The zeolite has the X-ray diffraction pattern set forth in Table 1 and its detailed diffraction pattern is shown in Table 3. The zeolite has a silica to alumina ration of 53, a La content of 2.50% by weight and a weight ratio of the moiety having the crystalline structure of ZSM-5 to the moiety having the crystalline structure of ZSM-11 of 30:70. In this zeolite, the unit cell parameters of the crystalline structure of ZSM-5 are as follows: $a=2.0118\text{nm}$, $b=1.9970\text{nm}$, $c=1.3426\text{nm}$, and the unit cell volume $V=5.393 \text{ nm}^3$; the unit cell parameters of the crystalline structure of ZSM-11 are as follows: $a=b=1.9989\text{nm}$, $c=1.3420\text{nm}$, and the unit cell volume $V=5.362\text{nm}^3$. The adsorption capacities of the zeolite towards n-hexane, cyclohexane and water are 10.2%, 4.1% and 6.0% by weight, respectively.

Example 2

Preparation of the La - ZSM-5/ZSM-11 cocrystalline zeolite of the invention by using trimethylene diamine as template

600 ml of water glass (the same as that in Example 1), 420 ml of deionized water and 34 g of 98% trimethylene diamine were mixed homogeneously to give operating solution I.

3.5g of 98% $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, 77 ml of 4M H_2SO_4 , 3.3g of 99% $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$ and 380 ml of deionized water were mixed homogeneously to give operating solution II.

The above two operating solutions were mixed under vigorous stirring to form a gel. The stirring was continued for another 5 minutes, then the rotation rate was lowered to about 100 rpm. Crystallization was carried out at 180 °C under stirring for 56 hours.

The material from crystallization was rapidly cooled to room temperature. The resulting crystal was washed with deionized water until the pH was washed to be 8 to 9, filtered, and dried at 110 ± 10 °C for 10 hours to give the La - ZSM-5/ZSM-11 cocrystalline zeolite.

The zeolite has the X-ray diffraction pattern set forth in Table 1 and its detailed diffraction pattern is shown in Table 3. The zeolite has a silica to aluimina ratio of 180, a La content of 1.15% by weight and a weight ratio of the moiety having the crystalline structure of ZSM-5 to the moiety having the crystalline structure of ZSM-11 of 50:50. The adsorption capacities of the zeolite towards n-hexane, cyclohexane and water are 10.6%, 4.0% and 4.8% by weight respectively.

Example 3

Preparation of the RE - ZSM-5/ZSM-11 cocrystalline zeolite of the invention by using hexamethylene diamine as template

580 ml of water glass (the same as that in Example 1), 420 ml of deionized water and 58g of 98% hexamethylene diamine were mixed homogeneously to give operating solution I.

49.5g of water-containing AlPO_4 gel (containing 5.4% by weight of Al_2O_3), 74 ml of 4M H_2SO_4 , 13.4g of 98% $\text{RECl}_3 \cdot 6\text{H}_2\text{O}$ (wherein the weight ratio of La_2O_3 to Ce_2O_3 was 0.6) and 351 ml of deionized water were mixed homogeneously to give operating solution II.

The above two operating solutions were mixed under vigorous stirring to from a gel. The stirring was continued for

another 5 minutes, then the rotation rate was lowered to about 100 rpm. Crystallization was carried out at 110 °C under stirring for 16 hours. The system was again heated to 180 °C and the crystallization was continued under stirring for another 38 hours.

The material from crystallization was rapidly cooled to room temperature. The resulting crystal was washed with deionized water until the pH was washed to be 8 to 9, filtered, and dried at 110±10 °C for 10 hours to give the RE - ZSM-5/ZSM-11 cocrystalline zeolite.

The zeolite has the X-ray diffraction pattern set forth in Table 1 and its detailed diffraction pattern is shown in Table 3. The zeolite has a silica to alumina ratio of 35, a RE content of 4.50% by weight, and a weight ratio of the moiety having the crystalline structure of ZSM-5 to the moiety having the crystalline structure of ZSM-11 of 40:60. The adsorption capacities of the zeolite towards n-hexane, cyclohexane and water are 9.8%, 3.2% and 6.5% by weight, respectively.

Example 4

Preparation of the La - ZSM-5/ZSM-11 cocrystalline zeolite of the invention by using the mixture of ethylene diamine and hexamethylene diamine as template

400 ml of water glass (containing 223g/l of SiO₂; 70.4g/l of Na₂O), 326 ml of deionized water, 13g of 98% ethylene diamine and 21g of 98% hexamethylene diamine were mixed homogeneously to give operating solution I.

11.5g of 99% Al₂(SO₄)₃ · 18H₂O, 67 ml of 4M H₂SO₄, 11g of 99% LaCl₃ · 6H₂O and 370 ml of deionized water were mixed homogeneously to give operating solution II.

The above two operating solutions were mixed under vigorous stirring to form a gel. The stirring was continued for another 5 minutes, then the rotation rate was lowered to about 100 rpm. Crystallization was carried out at 170 °C under stirring for 70 hours.

The material from the crystallization was rapidly cooled to room temperature. The resulting crystal was washed with deionized water until the pH was washed to be 8 to 9, filtered, and dried at 110±10 °C for 10 hours to give the La - ZSM-5/ZSM-11 cocrystalline zeolite.

The zeolite has the X-ray diffraction pattern set forth in Table 1 and its detailed diffraction pattern is shown in Table 3. The zeolite has a silica to alumina ratio of 60, a La content of 5.20% by weight, and a weight ratio of the moiety having the crystalline structure of ZSM-5 to the moiety having the crystalline structure of ZSM-11 of 60:40. The adsorption capacities of the zeolite towards n-hexane, cyclohexane and water are 11.7%, 3.0% and 5.3% by weight, respectively.

Table 3

Example 1		Example 2		Example 3		Example 4	
d(Å)	100I / I ₀	d(Å)	100I / I ₀	d(Å)	100I / I ₀	d(Å)	100I / I ₀
11.182	34	11.225	35	11.224	31	11.230	36
10.017	28	10.065	29	10.063	28	10.081	30
5.960	7	6.010	6	6.005	8	6.017	9
4.390	16	4.389	17	4.386	15	4.387	16
4.291	15	4.300	16	4.289	12	4.295	13
3.885	100	3.865	100	3.853	100	3.862	100
3.821	56	3.823	53	3.824	54	3.825	55
3.731	46	3.733	44	3.732	57	3.734	46
3.647	21	3.649	24	3.650	23	3.651	26
3.360	10	3.355	10	3.350	12	3.358	11
3.065	12	3.063	13	3.056	12	3.057	11
2.975	10	2.994	11	2.998	15	2.997	13
2.965	10	2.964	10	2.963	13	2.965	12
2.011	11	2.016	12	2.017	12	2.016	12
2.004	12	2.003	11	2.009	11	2.008	12

Example 5

5 This example illustrates that the rare earth-containing cocrystalline zeolite of the invention has good acid hydrothermal stability.

Four samples of the zeolites prepared in Examples 1 to 4 were calcined at 540 °C for 5 hours to remove organic amine template, then were ammonium ion exchanged with a mixed solution of 0.8 N NH_4NO_3 and 0.1N NH_4OH , respectively. The ion exchanged zeolites were washed with deionized water until no NO_3^- could be detected, filtered and then dried at 110 ± 10 °C for 24 hours to give ammonium form samples with a sodium content of less than 0.05% by weight. The ammonium form samples were converted to hydrogen form by calcining at 540 °C for 4 hours.

The hydrogen form samples were calcined at 550 ± 20 °C in the presence of 100% steam for 4 hours. Water fed into the calciner was 5 to 10 ml/g sample per hour.

15 The changes of the acid amounts of the samples before and after hydrothermal treatment were determined by ammonia adsorption-temperature programming desorption (TPD) respectively wherein helium at a flow rate of 20 ml/min was used as carrier gas. A sample was preactivated in the adsorption tube at 600 °C for 45 minutes, then cooled to 150 °C, to which was injected ammonia at constant temperature for adsorption. After saturation of adsorption, the sample was purged for 30 minutes, and the desorption of ammonia was carried out at a temperature-rise rate of 20 °C/min. The signal of ammonia desorbed at a specific temperature range was recorded by a chromatograph and the amount of acid sites of the sample was calculated by area normalization method with the result shown in Table 4.

20 In Table 4, the total amount of acid sites was calculated from the signal of ammonia desorbed at the desorption temperature of 200 to 600 °C. "Acid sites of medium strength %" referred to the percentage content of the amount of acid sites of medium strength after hydrothermal treatment based on the total amount of the acid sites, and the amount of acid sites of medium strength was calculated from the signal of ammonia desorbed at the desorption temperature of 320 to 450 °C.

25 As can be seen from the data in Table 4, the rare earth-containing cocrystalline zeolite of the invention has good acid hydrothermal stability, which has great industrial application significance with respect to the catalytic process involving hydrothermal treatment such as the regeneration of catalysts.

Table 4

Zeolite	Relative Amount of Total Acid Sites		Acid Sites of Medium strength %
	Before Hydrothermal Treatment	After Hydrothermal Treatment	
Example 1	100	91	66
Example 2	100	86	60
Example 3	100	88	57
Example 4	100	92	62

Example 6

45 This example illustrates the use of the zeolite of the invention in the alkylation of benzene with diluted ethylene.

The zeolite of Example 1 was mixed with alumina trihydrate at a weight ratio of zeolite (dry base): Al_2O_3 =65:35. To the mixture was added a suitable amount of 20% nitric acid and sesbania powder, mixed and kneaded, and then extruded to form granules of $\phi 2 \times 2 - 3$ mm. The granules were dried at 110 to 120 °C for 24 hours and were calcined at 450 °C for 1 hour, at 500 °C for 1 hour and at 540 °C for 5 hours. After cooling, the zeolite of the catalyst was converted to hydrogen form by ion exchanging with ammonium ions and calcining as described in Example 5; and the resulting catalyst sample of hydrogen form was hydrothermally treated at 550 ± 20 °C in the presence of 100% steam for 4 hours as described in Example 5.

55 5ml of the above catalyst sample after hydrothermal treatment was charged into a 10 ml continuous flow fixed bed reactor to carry out the alkylation of benzene with diluted ethylene. The raw material diluted ethylene gas was composed of 20% of ethylene, 20% of hydrogen and 60% of nitrogen by volume. The alkylation was carried out at a temperature of 370 °C, a pressure of 0.7MPa, a weight hourly space velocity of ethylene of 1.0 hr^{-1} and a mole ratio of

benzene to ethylene of 5. The results of the alkylation were as follows: the conversion of ethylene was 98.8%; the selectivity to the product ethylbenzene was 91.5%; and the selectivity of the alkylation was 99.0%, based on the total yield of ethylbenzene and diethylbenzene.

5 Example 7

This example illustrates the use of the zeolite of the invention in the alkylation of benzene with ethylene in the dry gas of catalytic cracking.

A post hydrothermal treatment zeolite catalyst sample of hydrogen form was prepared as described in Example 6.
 10 100 ml of the above catalyst sample was charged into a 200 ml adiabatic continuous flow fixed bed reactor, and the alkylation of benzene was carried out by using dry gas of catalytic cracking as raw material. The dry gas of catalytic cracking was composed of 33.0% of methane, 19.5% of ethylene, 16.0% of ethane, 14.0% of hydrogen, 10.2% of nitrogen, 4.0% of carbon dioxide, 1.5% of carbon monoxide, 0.8% of oxygen, 0.8% of propylene, 0.2% of propane by volume and 3500 mg/m³ of hydrogen sulfide and 1500 ppm water. The alkylation was carried out at an inlet temperature of the
 15 reactor of 350 °C, an outlet temperature of the reactor of 425 °C, a pressure of 0.7 MPa (gauge), a weight hourly space velocity of ethylene of 1.0 hr⁻¹ and a mole ratio of benzene to ethylene of 5. The reactor was continuously run for 45 days. The conversion of ethylene was maintained at 99 to 95%, the conversion of propylene was maintained at above 90%, and the selectivity of the alkylation based on the total yield of ethylbenzene and diethylbenzene was maintained at about 99%. An alkylation selectivity of 99% could be maintained after continuous running of the catalyst for 65 days
 20 when the conversion of ethylene was controlled at above 92%.

Example 8

This example illustrates the use of the zeolite of the invention in the aromatization of alkane.

25 Zeolite/alumina granules were prepared and calcined at 450 °C, 500 °C and 540 °C as described in Example 6, then were ion exchanged with ammonium ions as described in Example 5. The resulting zeolite catalyst of ammonium form was impregnated in an aqueous zinc nitrate solution at room temperature for 12 hours, filtered, dried at 110 ± 10 °C for 6 hours and calcined at 500 °C for 3 hours. The resulting zeolite catalyst of zinc form was then treated at 550 ± 20 °C in the presence of 100% steam for 4 hours as described in Example 5. The catalyst sample contains 2.0% by weight of
 30 zinc.

5 ml of the above catalyst sample was charged into a 10 ml continuous flow fixed bed reactor to carry out the aromatization of propane. The aromatization was carried out at a temperature of 500 °C, a pressure of 1 atm and a weight hourly space velocity of propane of 1.5 hr⁻¹. The results of the aromatization were as follows: the once-through conversion of propane was 75%, the selectivity to aromatics was 58% by weight, and the weight ratio of benzene: toluene: xylene was 1:0.9:0.4.
 35

Similar results were obtained when the zeolite catalyst was modified by gallium nitrate instead of zinc nitrate and a catalyst sample containing 2.0% by weight of gallium was used in the above aromatization of propane.

Example 9

40 This example illustrates the use of the zeolite of the invention in the conversion of methanol to light olefins.

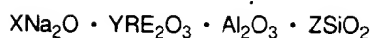
A zeolite catalyst of hydrogen form was prepared as described in Example 6, and a catalyst sample containing 2.4% by weight of magnesium was prepared according to the modification method described in Example 8 by substituting magnesium nitrate for zinc nitrate.

45 5 ml of the above catalyst sample was charged into a 10 ml continuous flow fixed bed reactor to carry out the conversion of methanol. The conversion was carried out at a temperature of 500 °C, a pressure of 1 atm and a weight hourly space velocity of methanol of 1.5 hr⁻¹. The results of the conversion were as follows: the conversion of methanol was 100%, and the yield of hydrocarbons in the product was 99.5%, wherein methane comprised 0.50%, ethylene comprised 16.75%, propylene comprised 54.70% and butylene comprised 20.30%, with the balance being C₂-C₄ alkane.
 50

Claims

1. A rare earth-containing crystalline aluminosilicate zeolite, characterized by

- 55 (1) having a cocrystalline structure of ZSM-5 and ZSM-11, wherein the weight ratio of the moiety having the crystalline structure of ZSM-5 to the moiety having the crystalline structure of ZSM-11 is 0.1 to 10;
 (2) having, in its originally synthesized anhydrous state, a chemical formula in terms of mole ratios of oxides as follows:



wherein $X=0.1-1.0$,
 $Y=0.01-1.0$, and
 $Z=20-300$;

(3) having the X-ray diffraction pattern set forth in Table 1; and

(4) having adsorption capacities towards n-hexane, cyclohexane and water of 9 to 11%, 3 to 5% and 4 to 8% by weight, respectively.

2. The zeolite according to claim 1, wherein said rare earth may be a single rare earth element or mixtures thereof.
3. A process for preparing the zeolite according to claim 1, characterized by mixing a homogeneous mixture I composed of water glass, a C_2-C_8 diamine and water with a homogeneous mixture II composed of an aluminium source, a mineral acid, a salt of rare earth element and water under vigorous stirring to form a gel, then crystallizing the gel under stirring at a temperature of 100 to 200 °C for 0.5 to 4 days, followed by rapidly cooling to room temperature and washing with water until a pH of 8 to 9, and finally drying, wherein the mole ratios of the above raw materials are as follows: Na_2O/Al_2O_3 : 7-12; RE_2O_3/Al_2O_3 : 0.01-1.0; SiO_2/Al_2O_3 : 30-600; H_2O/SiO_2 : 20-100; and the amine / SiO_2 : 0.1-0.5.
4. The process according to claim 3, wherein said diamine is selected from any one or a mixture of two of C_2-C_8 primary diamines.
5. The process according to claim 3, wherein said aluminium source is selected from a group comprising aluminium chloride, aluminium bromide, aluminium nitrate, aluminium sulfate and aluminium phosphate.
6. The process according to claim 3, wherein said mineral acid is selected from a group comprising sulfuric acid, hydrochloric acid, nitric acid and phosphoric acid.
7. The process according to claim 3, wherein said salt of rare earth element is selected from a chloride, nitrate and sulfate salt of a single rare earth element or a mixture thereof.
8. Use of the zeolite according to claim 1 as catalyst in the alkylation of aromatics.
9. Use of the zeolite according to claim 1 as catalyst in the aromatization of alkanes.
10. Use of the zeolite according to claim 1 as catalyst in the conversion of methanol to light olefins.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN 95/00099

A. CLASSIFICATION OF SUBJECT MATTER		
C01B 39/36, C01B 39/04, B01J 29/04		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
C01B 39/36, C01B 39/04, B01J 29/04		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
CA		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
DIALOG CAPS WPI		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4229424 (George T. Kokotailo, Woodbury, N. J.) 21. Oct. 1980 (21. 10. 80)	1, 2
A	US 4495166 (Robert B. Calvert, Plainsboro; Louis D. Rollmann, Princeton, both of N. J.) 22. Jan. 1985 (22. 01. 85)	3
A	EP 0000669 (Rollmann, Valyocsik) 07. Feb. 1979 (07. 02. 79)	1, 5, 7
A	EP 0550917 (Shu Xingtian, Fuwei, He Mingyan, Zhou Meng, Shi Zhicheng, Zhang Shuqin) 14. Jul. 1993 (14. 07. 93)	1, 2
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claims (s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>		
Date of the actual completion of the international search		Date of mailing of the international search report
08. Feb. 1996 (08. 02. 96)		07 MAR 1996 (07. 03. 96)
Name and mailing address of the ISA/ Chinese Patent Office, 6 Xitucheng Rd. Jimen Bridge, Haidian District, 100088 Beijing, China		Authorized officer
Facsimile No. (86-1)2019451		Telephone No. 2093904

INTERNATIONAL SEARCH REPORT
Information patent family members

International application No.

PCT/CN 95/00099

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4229424	21. 10. 1980	EP 0018090	80-10-29
		JP 55144413	80-11-11
		BR 8002149A	81-03-10
		ZA 802086A	81-04-29
		NZ 193384A	82-03-16
US 4495166	22. 01. 1985	ZA 8305250A	85-03-27
		CA 1202609A ₁	86-04-01
		NZ 204841A	86-05-09
		EP 101183B ₁	87-03-18
		AU 561835B ₂	87-05-21
EP 0000669	01. 08. 1978	IT 1097569A	85-08-31
		JP 54052699A ₂	79-04-26
		US 4108881A	78-08-22
		AU 515825B ₂	81-04-30
		ZA 784360A	80-03-26
		CA 1119146A ₁	82-03-02
EP 0550917	14. 07. 1993	none	